PYROLYSIS AND CATALYTIC CRACKING OF MUNICIPAL PLASTIC WASTE FOR RECOVERY OF GASOLINE RANGE HYDROCARBONS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

in

Chemical Engineering

By

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&

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CERTIFICATE

This is to certify the thesis entitled, "Pyrolysis And Catalytic Cracking Of Municipal Plastic Waste For Recovery Of Gasoline Range Hydrocarbons" submitted by Sri Sarthak Das & Sri Saurabh Pandey in partial fulfillment of the requirements for the award of Bachelor of Technology in Chemical Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

Plastic is an indispensable part of our daily life. Its production and consumption has been rising very rapidly due to its wide range of application. Due to its non biodegradable nature it cannot be easily disposed off. So, nowadays new technology is being used to treat the waste plasic. One of such process is pyrolysis. This paper describes non catalytic pyrolysis and catalytic cracking of plastic wastes into useful gasoline range hydrocarbons. Under the pyrolytic and cracking conditions the plastic wastes can be decomposed into three fractions: gas, liquid and solid residue. Here the main consideration is the recovery of liquid products which are composed of higher boiling point hydrocarbons. The waste plastics consisting of high density polyethylene (HDPE) was pyrolyzed in this study. Pyrolysis appears to be a technique that is able to reduce a bulky, high polluting industrial waste while producing energy and/or valuable chemical compounds. The pyrolysis of plastic wastes produces a whole spectrum of hydrocarbons including paraffins, olefins, naphthalenes and aromatics. By catalytic cracking more aromatics and naphthene in the range of C6-C8 which are valuable gasoline range hydrocarbons can be produced. Different catalysts like Silica Alumina, Modernite and Activated Carbon were used for catalytic cracking. The catalysts were used in different ratios with feed to find out the optimum range at which maximum yield occurs. The liquid product yield is about 60% in all the cases. In thermal pyrolysis, the product obtained gets solidified but in catalytic cracking good liquid product can be obtained which can be used as fuel. This application is further combined with technologies of municipal plastic wastes collection, classification and pretreatment at front end and product purification and testing at back end to determine the properties of the various products obtained.

Chapter 1

Introduction

Introduction

A marvel of polymer chemistry, plastics has become an indispensable part of our daily life. Although plastics are a newer discovery, they have become a part of everyday consumer life and its production and consumption have increased drastically. Plastic have molded the modern world and transformed the quality of life. There is no human activity where plastics do not play a key role from clothing to shelter, from transportation to communication and from entertainment to health care [5]. Plastics have become an indispensable part in today's world. Due to their light-weight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in entire gamut of industrial and domestic areas. [1]

Plastics are non-biodegradable polymers mostly containing carbon, hydrogen, and few other elements such as chlorine, nitrogen etc. Due to its non-biodegradable nature, the plastic waste contributes significantly to the problem of Municipal Waste Management. The production of plastics is significantly growing. Nowadays the plastic production is more than 200MT worldwide annually. [2] The per capita consumption of plastics from a last few decades is increasing rapidly; it is shown in the table 1.1 the status of per capita consumption of plastics in some selected countries worldwide [8].

Table 1.1: Per capita Consumption of Plastics in Some Selected Countries of the World.

Country	**Per Capita Consumption** in Kg.
India (1998)	1.6
India (2000)	4.0
Vietnam	1.5
China	6.0
Indonesia	8.0
Mexico	13.0
Thailand	18.0
Malaysia	22.0
Western Europe	60.0
Japan	70.0
North America	78.0

According to a nation wide survey, conducted in the year 2004, approximately 10,000 tones (ten thousand tones) of plastic waste were generated every day in our country, and only 60% of it was recycled, balance 40% was not possible to dispose off. So gradually it goes on accumulating, thereby leading to serious disposal problems. [1]. Plastic is derived from petrochemical resources. In fact these plastics are essentially solidified oil. They therefore have inherently high calorific value. The calorific values of some of the plastic materials along with coal are shown in table1.2 [7].

Table 1.2: Calorific Values of Some Plastic Materials.

Material	**Btu per pound**	**Kilojoules per kilo**
Coal	11,500	27,000
Polyethylene	20,000	46,500
Polypropylene	19,300	45,000
Polystyrene	17,900	41,600
PET	9,290	21,600
PVC	8,170	19,000

Theoretically this energy can be captured and transformed into other useful forms. It is a well-known fact that energy can neither be created nor destroyed but merely transformed.
One of the most common methods of transforming energy from for example, a solid to another form is thermal treatment. Through the various methods of thermal treatment one
may obtain heat, electricity or chemicals suitable for other applications [7].

Waste Plastics are mostly land filled or incinerated; however, these methods are facing great social resistance because of environmental problems such as air pollution and soil contamination, as well as economical resistance due to the increase of space and disposal costs [3]. In a long term neither the land filling nor the incineration solve the problem of wastes, because the suitable and safe depots are expensive, and the incineration stimulates the growing emission of harmful and greenhouse gases e.g. NOx, SOx, COx etc [6]. Accordingly, recycling has become an

important issue worldwide. This method can be classified as energy recovery, material recycling and chemical recycling. Among them one of the prevalent alternative methods is the production of converted fuel and chemicals by means of the thermal or catalytic degradation of polymers [4].

Plastics pyrolysis, on the other hand, may provide an alternative means for disposal of plastic wastes with recovery of valuable liquid hydrocarbons. In pyrolysis or thermal cracking, the polymeric materials are heated to high temperatures, so their macromolecular structures are broken down into smaller molecules and a wide spectrum of hydrocarbons are formed. These pyrolytic products can be divided into a gas fraction, a liquid fraction consisting of paraffins, olefins, naphthenes and aromatics (PONA), and solid residues. In catalytic cracking, more aromatics and naphthenes are selectively formed in the presence of commercial fluid cracking catalysts (FCC) or reforming catalysts, so that the productivity and economics of pyrolysis processes are improved. [5] Cracking was realized both in the batch and continuous systems. It was also examined that the results obtained by batch cracking are useable to the continuous reactor planning. The goal of these experiments was the developing of a waste free so-called green technology [6].

The main objective of this study was to investigate the effect of catalyst amount, reaction temperature, plastic type (especially HDPE) and weight ratio of waste plastic to catalyst, with a semi-batch reactor, based on the results of yields and yield distributions of liquid product as a function of lapsed time. The objective was also to study the product yields and their distribution with different types of catalysts (Silica Alumina, Activated Carbon and Mordenite) in the catalytic degradation of waste plastics with respect to time and temperature. Along with this the main objective was to find out the best catalyst for the catalytic cracking process.
One more objective is quantitative analysis of gaseous, liquid and solid products from thermal and catalytic degradation of HDPE and the comparison of the physical properties of the liquid products and to suggest the best reactor design along with the economical factors effecting the commercialization of this technique.

Chapter 2

Literature Review

2.1 Plastics

Plastics are macromolecules, formed by polymerization and have the ability to be shaped by the application of reasonable amount of heat and pressure or some other form of force [10].

Polymerization is the process by which individual units of similar or different molecules ("mers") combine together by chemical reactions to form large or macromolecules in the form of long chain structures, having altogether different properties than those of starting molecules ("mers"). Several hundreds and thousands of "mers" combine together to form the macromolecules, that we call polymers.

Depending upon their nature and properties, the polymers are classified as Plastics, Rubbers or Elastomers and Fibres.

There are mainly two types of Plastics: Thermoplastics and Thermosetting Plastics

Thermoplastics are those, which once shaped or formed, can be softened by the application of heat and can be reshaped repeatedly, till it looses its property.

Example: Polyethylene, Polypropylene, Nylon, Polycarbonate etc.

Applications are: Polyethylene Buckets, Polystyrene Cups, Nylon ropes etc.

Thermosetting Plastics are those, which once shaped or formed, cannot be softened by the application of heat. Excess heat will char the material.

Example: Phenol formaldehyde, Urea Formaldehyde, Melamine Formaldehyde, Thermosetting Polyester etc.

Applications are: Backelite Electrical switches, Formica / sermica table tops, melamine Cutlery.

2.1.1 Physical Properties of Plastics[9]

Plastics have physical characteristics, which need to be considered when processing any product. The following table contains physical data for several commercially available plastics.

Plastic	Thermal Properties				Strength		Density
Abbreviation (chemical name) Brand name	Tm °C	Tg °C	Td °C	Cte ppm/°C	Tensile psi	Compressive psi	g/cc
ECTFE (ethylene chlorotrifluoro ethylene copolymer)	220 245		116	80	6000 7000		1.68- 1.69

ETFE (ethylene tetrafluoro-ethylene copolymer) Tefzel	270		104	59	6500	7100	1.7
FEP (fluorinated ethylene-propylene copolymer) Teflon FEP	275		70		2700 3100	2200	2.12-2.17
PFA (perfluoroalkoxy) Teflon PFA	310		74		4000 4300		2.12-2.17
PCTFE (polychlorotrifluoro-ethylene)	220		125	36 70	4500 6000	4600 7400	2.08-2.2
PTFE (polytetrafluoroethylene) Teflon	327		121	70 120	2000 5000	1700	2.14-2.20
PVF (polyvinylfluoride) Tedlar						7000 18000	1.38-1.57
PVDF (polyvinylidenefluoride) Kynar	174 178		138	70 142	5200 7250	10900 14000	1.77-1.78
(polycaprolactam) Nylon6	210 220		185 190	80 83	7400	13000 16000	1.12-1.14
PC (polycarbonate) Lexan		150	138	68	9500	12500	1.2
PET (polyethyleneterephthalate) Mylar	245 265	73 80	21 38	65	7000 10500	11000 15000	1.29-1.40
LDPE (low density polyethylene)	98 115	-25	40 44	100 220	1200 4550		0.917-0.932
LLDPE (linear low density polyethylene)	122 124				1900 4000	0	0.918-0.940
HDPE (high density	130		79	59	3200	2700	0.952-

polyethylene)	137		91	110	4500	3600	0.965
UHMWPE (ultra high molecular weight polyethylene)	125 135		68 82	130	5600		0.940
PI (polyimide)		310 365	277 360	45 56	10500 17100	30000 40000	1.36- 1.43
PMMA (polymethylmethacrylate) Plexiglas		85 105	79 107	50 90	7000 11000	10500 18000	1.17- 1.20
PP (polypropylene)	168 175	-20	107 121	81 100	4500 6000	5500 8000	0.900- 0.910
PS (polystyrene) Styron		74 105	68 96	50 83	5200 7500	12000 13000	1.04- 1.05
PVC (polyvinylchloride)		75 105	57 82	50 100	5900 7500	8000 13000	1.30- 1.58
PVDC (polyvinylidenechloride) Saran	172	-15	54 66	190	3500 5000	2000 2700	1.65- 1.72

Table 2.1: Physical properties of plastics.

Here, Tm- crystalline melting temperature (some plastics have no crystallinity and are said to be amorphous).

Tg-glass transition temperature (the plastic becomes brittle below this temperature).

Td- heat distortion temperature under a 66 psi load.

Cte-coefficient of linear thermal expansion.

Tensile Strength is the load necessary to pull a sample of the plastic apart.

Compressive Strength is the load necessary to crush a sample of the plastic.

Density or specific gravity is the mass of plastic per unit volume.

2.1.2 Types of Waste Plastics & Their Recyclability

The following table shows different types waste plastics and their recyclability with standard mark for recycling to identify easily with many examples.

Table 2.2: Types of waste plastics and their recyclables: [13]

Mark	TYPE	RECYCLABLE	ABBREVIATION	DESCRIPTION
	Type 1	Yes	PET	Polyethylene Terephthalate Beverages.
	Type 2	Yes	HDPE	High-Density Polyethylene Milk, detergent & oil bottles, toys, containers used outside, parts and plastic bags.
	Type 3	Yes, but not common	V/PVC	Vinyl/Polyvinyl Chloride Food wrap, vegetable oil bottles, blister packages or automotive parts.
	Type 4	Yes	LDPE	Low Density Polyethylene, Many plastic bags, shrink-wraps, garment bags or containers.
	Type 5	Yes	PP	Poly Propylene. Refrigerated containers, some bags, most bottle tops, some carpets, and some food wrap.
	Type 6	Yes, but not common	PS	Polystyrenes. Through away utensils, meatpacking, protective packing.
	Type 7	Some	_____	OTHER. Usually layered or mixed plastic.

2.1.3 Recycling – Effect of Contamination:

In polymers used for recycling, contamination is omnipresent, resulting in reduction of the quality of recycling. It can be in the form of dirt, printing inks, paper, metals, foil, additives, pesticides, partially oxidized polymers, contamination by foreign bodies can be noticed even in PET and HDPE bottles collected from roadsides. In very old scraps of building products, electrical and electronic system, vehicles, furniture etc., which now come for recycling may contain very high concentration of additives in particular, fire retardants, which are now banned. Contamination can be reduced if consumers can be organized to segregate polymer products before disposal. However accidental or unintentional mixtures, multi-component products etc do pose problems.

Table 2.3: Common contaminants in recycled polymers[9]

Polymer	**Recycle source**	**Contamination**
PET	Beverage bottles	PVC, green PET, Al, water, glue, oligomers
HDPE	Milk/water bottles	PP, milk residue, pigments, paper, EPS, cork
LDPE	Greenhouse films	Insecticides, soil, Ni, oxidation products
LDPE	Shopping bags	Paper receipts, printing ink, food scraps
PP	Battery cases	Pb, Cu, acid, grease, dirt
HDPE	Detergent bottles	Paper, glue, surfactants, bleach, white spirit
PET	Photographic film	Silver halides, gelatin, caustic residues
Phenolic	Circuit boards	Cu, tetrabromobisphenol A
LDPE	Multi layer film	Ethylene vinyl alcohol, polyamide, ionomer
PVC	Beverage bottles	PET, PE, paper, Al foil, PP
ABS	Appliance housings	Polybrominated flame retardants
SBR	Automobile tires	Steel wire, fiber, oil extender
LDPE	Mulch film	Soil (up to 30%), iron (up to 3% in soil)

The simple and widely used process for separation is by using differences in density, e.g. HDPE Cups and PET bottles.

Separation and purification by chemical reaction process will give better results. Mixtures of solvents allowing selective dissolution can be used for multi component plastic products.

2.1.4 Sources of Waste Plastics

Plastic wastes can be classified as industrial and municipal plastic wastes according to their origins; these groups have different qualities and properties and are subjected to different management strategies.

Industrial plastic wastes:

Industrial plastic wastes are those arising from the plastics manufacturing and processing industry. Usually they are homogeneous or heterogeneous plastic resins, relatively free of contamination and available in fairly large quantities. For industrial plastic wastes, repelletization and remolding seem to be a simple and effective means of recycling. But when plastic wastes are heterogeneous or consist of mixed resins, they are unsuitable for reclamation. In this case thermal cracking into hydrocarbons may provide a suitable means of recycling, which is termed chemical recycling.

Municipal plastic wastes:

Municipal plastic wastes normally remain a part of municipal solid wastes as they are discarded and collected as household wastes. Plastics usually account for about 7% of the total MSW by weight and much more by volume. In order to recycle municipal plastic wastes, separation of plastics from other household wastes is required. Although MSW separation technologies have been studied extensively, it is still not possible to classify MSW mechanically and obtain marketable fractions. So for recycling of municipal plastic wastes, waste separation is required at the household. For this reason the household wastes are separately disposed into three parts:

(1) Combustibles such as paper, kitchen waste, textiles, and wood,

(2) Incombustibles such as metals, glass, ceramics, and

(3) Plastics, then the collected plastics will be mixed plastic wastes with major components of PE, PP, PS, PVC, etc.

2.2. Recycling techniques of waste plastics: [13]

Basically there are 4 different ways of recycling of plastics: [9]

1. **Primary Recycling** – Conversion of waste plastics into products having performance level comparable to that of original products made from virgin plastics. These methods are undergone in to material recycling methods.

2. **Secondary Recycling** – Conversion of waste plastics into products having less demanding performance requirements than the original material. These are also a part of material recycling methods.

3. **Tertiary Recycling –** The process of producing chemicals / fuels / similar products from waste plastics. These methods are known as chemical recycling or feedstock recycling methods.

4. **Quaternary Recycling** – The process of recovering energy from waste plastics by incineration.

Plastics recycling will cover a wide range of different methods. The main areas are given below.

- **I.** Material recycling
- **II.** Energy recycling
- **III.** Chemical Recycling

Combinations of these are well known and in are use to some extent. In all these methods is common that the yield of organic material is not more than the input of plastic waste material.

2.2.1. Material recycling of waste Plastics [5]

Initial upgrading: Once the plastic has been collected, it will have to be cleaned and sorted. The techniques used will depend on the scale of the operation and the type of waste collected, sorting of plastics can be by polymer type (thermo set or thermoplastic for example), by product (bottles, plastic sheeting, etc.), by color, etc

Size reduction techniques: Size reduction is required for several reasons; to reduce larger plastic waste to a size manageable for small machines, to make the material denser for storage and transportation, or to produce a product, which is suitable for further processing. There are several techniques commonly used for size reduction of plastics.

Cutting: It is usually carried out for initial size reduction of large objects. It can be carried out with scissors, shears, saw, etc.

Shredding: It is suitable for smaller pieces. A typical shredder has a series of rotating blades driven by an electric motor, some form of grid for size grading and a collection bin. Materials are fed into the shredder via a hopper, which is sited above the blade rotor. The product of shredding is a pile of coarse irregularly shaped plastic flakes, which can then be further processed.

Agglomeration: It is the process of pre-politicizing soft plastic by heating, rapid cooling to solidify the material and finally cutting into small pieces. This is usually carried out in a single machine. The product is coarse, irregular grain, often called crumbs.

Further processing techniques:

Extrusion and palletizing: The process of extrusion is employed to homogenize the reclaimed polymer and produce a material that it subsequently easy to work. The reclaimed polymer pieces are fed into the extruder, are heated to induce plastic behavior and then forced through a die (see the following section on manufacturing techniques) to form plastic spaghetti, which can then be cooled in a water bath before being palletized.

Extrusion: The extrusion process used for manufacturing new products is similar to that outlined above for the process preceding pelletisation, except that the product is usually in the form of a continuous ‘tube’ of plastic such as piping or hose.

Injection moulding: The first stage of this manufacturing process is identical to that of extrusion, but then the plastic polymer emerges through a nozzle into a split mould. This type of production technique is used to produce moulded products such as plates, bowls, buckets, etc.

Blow moulding: Again the spiral screw forces the plasticized polymer through a die. This manufacturing technique is used for manufacturing closed vessels such as bottles and other containers.

Film blowing: Film blowing is a process used to manufacture such items as garbage bags. It is a technically more complex process than the others described in this brief and requires high quality raw material input. The process involves blowing compressed air into a thin tube of polymer to expand it to the point where it becomes a thin film tube. One end can then be sealed and the bag or sack is formed.

2.2.2. Energy Recycling

The two main alternatives for treating municipal and industrial polymer wastes are energy recycling, where wastes are incinerated with some energy recovery and mechanical recycling. The incineration of polymer waste meets with strong societal opposition. Here one incineration method is described for energy recovery from waste plastics including PVC.

Municipal Solid waste Incinerators: [4]

Municipal solid waste incinerators are a proven, robust technology for dealing with very different mixed waste types of different origin. The typical MSWI is built for dealing with waste of a caloric value between 9 and 13 MJ/kg. MSWI's are currently a default technology for the treatment of integral household waste in countries such as Denmark, Sweden, the Netherlands and Germany. In Europe, on average some 7% of this integral household waste consists of plastics.

Description of the process:

Municipal Solid Waste Incinerators (MSWIs) are in principle built for the treatment of municipal or similar industrial wastes. In such a kiln the waste, after it is tipped into storage and has been made more homogeneous, is transferred to a grid-type kiln. This rolling grid is placed under a certain slope, so that the waste is slowly transported with such a speed, that full incineration takes place. At the end of the grid slags remain. The slags are treated in order to recover the ferrous and non-ferrous fraction. Just like in the case of a rotary kiln, the flue gases pass through

cleaning equipment such as an electro filter, an acid scrubber, a caustic scrubber, an active carbon scrubber. In modern MSWIs, the energy is also recovered as much as possible. The flue gas cleaning process leads to fly ash and flue gas cleaning residue, which has to be land filled. A large fraction of the chlorine input into the MSWI ends up in the flue gas-cleaning residue. A process has been developed for the neutralization of flue gases with sodium bicarbonate. As such, this has no significant influence on the amount of flue gas cleaning residue generated. However, this residue can be treated at a separate plant recovering soda and salt. In that case, much lower residual amounts of hazardous waste have to be disposed of.

2.2.3. Chemical Recycling:

Feedstock recycling also known as chemical recycling or tertiary recycling, aims to convert waste polymers into original monomers or other valuable chemicals. These products are useful as feedstock for a variety of downstream industrial processes or as transportation fuels. The different routes of chemical recycling are shown below.

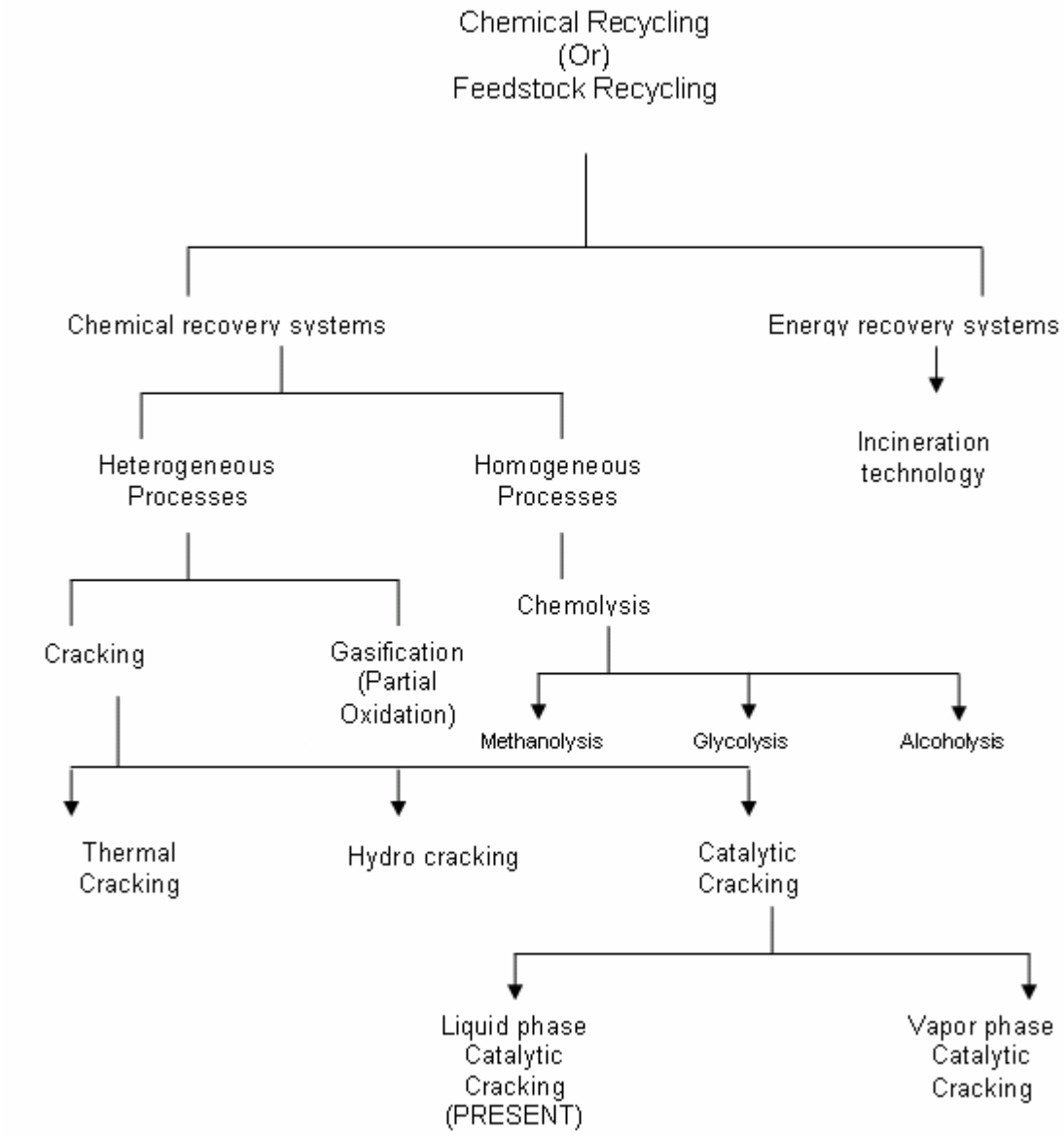


Fig 2.1: Ways of chemical recycling techniques.

2.2.3.1Chemolysis/ Solvolysis:

Individual plastics are chemically treated or depolymerized and turned back into monomers. Chemolysis uses chemical agents as catalysts for complete depolymerisation of plastic resins.

Chemolysis includes a range of processes such as glycolysis, hydrolysis, methanolysis, achoholysis, saponification dialysis etc.

Hydrolysis: [9]

Hydrolysis leads to direct recovery of the original raw materials by targeted reaction of water molecules at the linkage points of the starting materials. All hydrolysable plastics such as polyamides, polyesters, polycarbonates, polyureas, and polyurethanes are resistant to hydrolysis under normal conditions of use.

Hydrolysis of polyurethane foams is particularly interesting since they have a very low density (30 kg/m^3) and thus take up considerable storage space. Product yields are outstanding. Almost 100% of the polyether and ca. 90% of the amine can be recovered. The regenerated materials can be reused directly, together with fresh starting material, for the same foam material. Raw material in the waste can thus be fed back again to the same production process and the environment is thus not burdened by that quantity of waste material.

Alcoholysis: [9]

Chemical degradation polyurethanes can also be achieved by alcoholysis to give a polyhydroxy alcohol and small urethane fragments formed by transesterification. Carbon dioxide is not formed in this reaction. If a diol is used as the alcohol, then the urethane fragments also contain terminal hydroxyl groups. These polyhydroxy alcohols can be converted directly to polyurethane foam following the addition isocyanates and varying proportions of new polyhydroxy alcohols.

Glycolysis:

The degradation of polymers in the presence of glycol such as ethylene glycol or diethylene glycol is known as glycolysis. And in the presence of methanol it is known as Methanolysis.

2.2.3.2 Gasification or Partial oxidation: [3]

The direct combustion of polymer waste, which has a good calorific value, may be detrimental to the environment because of the production of noxious substances such as light hydrocarbons, NOx, sulfur oxides and dioxins. Partial oxidation (using oxygen and/or steam), however, could generate a mixture of hydrocarbons and synthesis gas (CO and H_2), the quantity and quality being dependent on the type of polymer used. A new type of waste gasification and smelting system using iron-making and steel-making technologies has been described by Yamamoto et al., reportedly to produce a dioxin-free and high-calorie purified gas. Hydrogen production efficiency of 60–70% from polymer waste has been reported for a two-stage pyrolysis and partial oxidation process. Co-gasification of biomass with polymer waste has also been shown to increase the amount of hydrogen produced while the CO content reduced. The production of bulk chemicals, such as acetic acid, from polyolefins via oxidation using NO and/or O_2, is also possible.

2.2.3.3 Cracking: [5]

Cracking processes break down polymer chains into useful lower molecular weight compounds. This can be achieved by reaction with hydrogen, known as hydrocracking or by reaction in an inert atmosphere (pyrolytic methods), which can be either thermal or catalytic cracking.

2.2.3.3.1 Hydro cracking:[5]

Hydro cracking of polymer waste typically involves reaction with hydrogen over a catalyst in a stirred batch autoclave at moderate temperatures and pressures (typically 423–673 K and 3–10 MPa hydrogen). The work reported, mainly focuses on obtaining a high quality gasoline starting from a wide range of feeds. Typical feeds include polyolefins, PET, polystyrene (PS), polyvinyl chloride (PVC) and mixed polymers, polymer waste from municipal solid waste and other sources, co-mixing of polymers with coal co-mixing of polymers with different refinery oils such as vacuum gas–oil and scrap tyres alone or co-processed with coal. To aid mixing and reaction, solvents such as 1-methyl naphthalene, tetralin and decalin have been used with some success.

Several catalysts, classically used in refinery hydrocracking reactions, have been evaluated and include transition metals (e.g., Pt, Ni, Mo, Fe) supported on acid solids (such as alumina, amorphous silica–alumina, zeolites and sulphated zirconia). These catalysts incorporate both cracking and hydrogenation activities and although gasoline product range streams have been obtained, little information on metal and catalyst surface areas, Si/Al ratio or sensitivity to deactivation is quoted.

2.2.3.3.2 Thermal cracking: [8]

Thermal cracking, or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 500- 800ºC and results in the formation of a carbonised char and a volatile fraction that may be separated into condensable hydrocarbon oil and a non-condensable high calorific value gas [1]. The proportion of each fraction and their precise composition depends primarily on the nature of the plastic waste but also on process conditions.
In the case of polyolefins like polyethylene or polypropylene, thermal cracking has been reported to proceed through a random scission mechanism that generates a mixture of linear olefins and paraffins over a wide range of molecular weights [1]. In other cases, like polystyrene and polymethylmetacrylate, thermal degradation occurs by a so-called unzipping mechanism that yields a high proportion of their constituent monomers [1].

In pyrolytic processes, a proportion of the species generated directly from the initial degradation reaction are transformed into secondary products due to the occurrence of inter and intramolecular reactions. The extent and the nature of these reactions depend both on the reaction temperature and also on the residence of the products in the reaction zone, an aspect that is primarily affected by the reactor design.
In addition, reactor design also plays a fundamental role, as it has to overcome problems related to the low thermal conductivity and high viscosity of the molten polymers. Several types of reactors have been reported in the literature, the most frequent being fluidised bed reactors [16-17], batch reactors [4, 18] and screw kiln reactors [1].
Pyrolysis and gasification of plastics and other carbonaceous fuels have been studied extensively in the past. Recent progress in converting plastic wastes into petrochemicals by means of

pyrolysis in the absence of a catalyst has been reviewed by Kaminsky[17,18,19]. Four types of mechanisms of plastics pyrolysis have been proposed:

(a) End-chain scission or depolymerization: The polymer is broken up from the end groups successively yielding the corresponding monomers.
(b) Random-chain scission: The polymer chain is broken up randomly into fragments of uneven length.
(c) Chain-stripping; Elimination of reactive substitutes or side groups on the polymer chain, leading to the evolution of a cracking product on one hand, and a charring polymer chain on the other.
(d) Cross-linking: Formation of a chain network, which often occurs for thermosetting polymers when heated.

These different mechanisms and product distributions are to some extent related to bond dissociation energies, the chain defects of the polymers, and the aromaticity degrees, as well as the presence of halogen and other hetero-atoms in the polymer chains. For common plastics the decomposition mechanisms and associated monomer yield are listed in Table 2. The pyrolysis of PS occurs by both end-chain and random chain scission and the monomer recovery is only some 45%. For PE and PP, the main components of municipal plastic wastes, the pyrolysis occurs through the random-chain scission mechanism and a whole spectrum of hydrocarbon products is obtained. The gas and oil yields from polyolefin pyrolysis are about 50 and 40% wt. of the feed at 750°C, respectively, and the oil fraction consists mainly of higher boiling point hydrocarbons (tar).

2.2.3.3.3 Catalytic cracking: [8]

A number of experimental studies have been carried out by various researchers with the objective of improving liquid hydrocarbons yield from plastics pyrolysis by introducing suitable catalysts. Common plastics such as PE and PP have already been tested extensively; the catalysts tested are mainly those used in the petrochemical refinery industry. The laboratory experimental

set-up in these studies is a mostly flow reactor; it may be useful to distinguish between two modes of catalyst usage: 'liquid phase contact' and 'vapor phase contact'. In 'liquid phase contact', the catalyst is contacted with melted plastics and acts mainly on the partially degraded oligomers from the polymer chains; in 'vapor phase contact', the polymer is thermally degraded into hydrocarbon vapors which are then contacted with the catalyst. The current project is developing for the production of liquid hydrocarbon fuel by the application of liquid phase contact catalytic cracking.

FCC Catalysts in Polyolefin Pyrolysis

FCC catalysts have been employed on an industrial scale in the petroleum refining industry and were developed mainly for cracking heavy oil fractions from crude petroleum into lighter and more desirable gasoline and liquid petroleum gas (LPG) fractions. The feedstock products fall under four major classes of HCs: Paraffins, Olefins, Naphthalenes and Aromatics (PONA distribution). Gasoline range fuels consist of paraffin and olefins in the C_5-C_{12} range [11]. Within aromatics, products of polyolefins, especially polystyrene, are grouped as BTX (benzene, toluene, and xylene). Recent reviews on the FCC process can be found in literature [12, 13, 14,15].Major commercial FCC catalysts are given in table 2.4 along with their composition.

Table 2.4: FCC Catalysts

Catalyst	Major cations exchanged	Composition (wt. %)				
		SiO_2	Al_2O_3	Na	Ca	Re
Silica-alumina	—	88–74	12–26	—	—	—
Zeolite A	Ca^{2+}	42.5	37.4	7.85	13.0	—
Zeolite X and Y	Ca^{2+}	47.8	31.5	7.7	12.3	—
	RE, NH_4^+	40.0	33.0	0.22	—	26.5
Zeolite ZK5	H^+	26.8	23.1	0.47	—	—
Mordenite	H^+	80.1	13.4	0.3	1.54	—

RE, rare earth metals.

The main effects of catalyst addition in plastics pyrolysis are as follows.

- The pyrolysis temperature for achieving a certain conversion is reduced drastically and as the catalyst/plastics ratio is increased, the pyrolysis temperature can be further lowered.[16]
- More iso-alkanes and aromatics in the C_5–C_{10} range can be produced which are highly desirable gasoline-range hydrocarbons.
- The reaction rate is increased significantly; e.g. the initial rate of degradation of polypropylene was reported to be approximately four times faster than that of non-catalytic thermal degradation [16]

2.3 Gasoline-range hydrocarbons

The pyrolysis of plastic wastes produces a whole spectrum of hydrocarbons including paraffin, olefins and aromatics. But all these hydrocarbons are not suitable for gasoline usage. Gasoline qualities are usually measured in terms of volatility and octane number of the hydrocarbons. For gasoline production, aromatics, naphthenes and isoalkanes are highly desirable, whereas olefins and n-paraffin are least desirable [3].

(a) Volatility: - Adequate volatility is required for smooth operation of petrol engines. Light hydrocarbons have higher volatilities than heavy hydrocarbons. They may cause vapor lock when the engine is hot. However heavy hydrocarbons have lower volatilities, but they may not be volatile enough to start the engine when the engine is cold. Suitable hydrocarbons are in the C_5–C_8 range. Some C_9 and above may be added according to climate and season.

(b) Octane number: -. This is a measure of the gasoline quality for prevention of early ignition which leads to cylinder knock. Higher octane numbers are preferred for internal combustion engines. The octane numbers of selected hydrocarbons are listed in Table-2.4

Table 2.5. Octane numbers and boiling points of some hydrocarbons [20,21]

Compounds	Octane number (blending, research method)	Boiling point (°C)
Paraffins		
n-Butane	113	0
n-Pentane	62	36
n-Hexane	19	69
n-Heptane	0	98
Isooctane	100	
2-Methylhexane	41	90
2,2-Dimethylpentane	89	
2,2,3-Trimethylbutane	113	
Naphthenes		
Cyclopentane	141	49
Methylcyclopentane	107	72
Cyclohexane	110	81
Olefins		
2-Methyl-1-hexene	91[a]	91
3-Methyl-2-pentene	97[a]	68
Aromatics		
Benzene	99	80
Toluene	124	111
m-Xylene	145	139
1,3-Dimethylbenzene	145	
1,3,5-Trimethylbenzene	171	
Isopropylbenzene	132	

[a] Actual octane number.

Accordingly, it is desirable that the pyrolytic conversion of plastic wastes produces more aromatics, naphthenes and iso-alkanes with carbon number in the range C_5–C_8.

Chapter 3

Experimental Method

3.1 Polymer Materials Collected

3.1.1 Collection of the waste plastic materials

The waste plastics used by me for the process consisted mainly of HDPE products in the form of used plastic disposable glasses. A person was allotted for collecting the material. He collected the glasses that were used by students during the time of semester examination and the various functions taking place in our college. Payment was made to him on a daily basis for his labor. The LDPE packaging bags used for the packaging of new computers was also used as raw materials.

The picture below shows the material, which we collected.

Fig 3.1: The waste plastic materials collected by us.

3.1.2 Preparation of HDPE & LDPE pellets.

The material that was collected was subjected to cutting by using scissors manually. This was done to increase the surface area of contact of the material during melting process. The material was then directly taken for the melting process. For this purpose a cylindrical stainless steel vessel of 27.2 cm diameter and 30 cm height was used. The weight of the vessel was 1395g. The vessel was put on an electrical domestic heater and a temperature of around 150°C was maintained for melting. Total time taken for single batch of reaction was around 15 minutes. The following table shows the composition of the final products of melting of a single batch.

Table 3.1: Product distribution of LDPE & HDPE materials from melting.

Material Used	**wt. of the material**	**wt. of final pellets**	**wt. of gases evolved**	**% age loss**
HDPE	200g	195g	5g	2.5
LDPE	300g	286g	14g	4.67

Continuous stirring was done during the process to avoid sticking of the plastic materials to the bottom of the vessel and for better distribution of heat. As the table above shows, the gases coming from the process are directed into the water bath. Here the gases are completely absorbed. According to literature the gases coming from the process are in the range of LPG and HCl gases [1]. But we were unable to collect the gases. During the stirring process, the lid of the vessel was opened intermittently. Then some of the gases escaped to the atmosphere. The molten plastic in liquid form was cooled to room temperature to obtain the solid form. Then the material was broken into small sizes in the range of 10mm-30mm. These pellets were ready for the pyrolysis process.

Fig 3.2. Stirring during the melting process

Fig 3.3. Absorption of gases in water bath

3.2 Pyrolysis

Pyrolysis or cracking processes break down polymer chains into useful lower molecular weight compounds. This can be achieved by the application of heat at atmospheric pressure in the absence of oxygen, which can be either thermal or catalytic cracking.

3.2.1 Thermal Pyrolysis

The molten waste plastic pellets were taken into a cylindrical cast iron reactor of 5.8 cm diameter and 11.2 cm height. The reactor was completely packed with the material. The reactor was perfectly sealed with M-Seal to prevent the leakage of vapors from the reactor. The reactor was put inside a furnace with the support of a stand. The reactor was placed inside the furnace such that it does not touch the side of the furnace and is uniformly heated from all the sides. The furnace used was muffle furnace made by SHIMADEN CO. LTD, Japan, coupled with SR1 and SR3 series digital controller. With the help of controller we set the process at different temperatures for different experiments. The rate of increase of temperature is 25°C/min.

The vapors coming from the reactor were passed through the pipeline connected to the top of the reactor from where it passes through a glass condenser as shown in the fig. Here condensation of the vapours takes place. Proper arrangement was made for the condensation by putting wet jute over the pipelines to support further condensation. Then the condensed liquids were collected. The non-condensable gases were very less and probably negligible in quantity because most of them were removed during melting process.

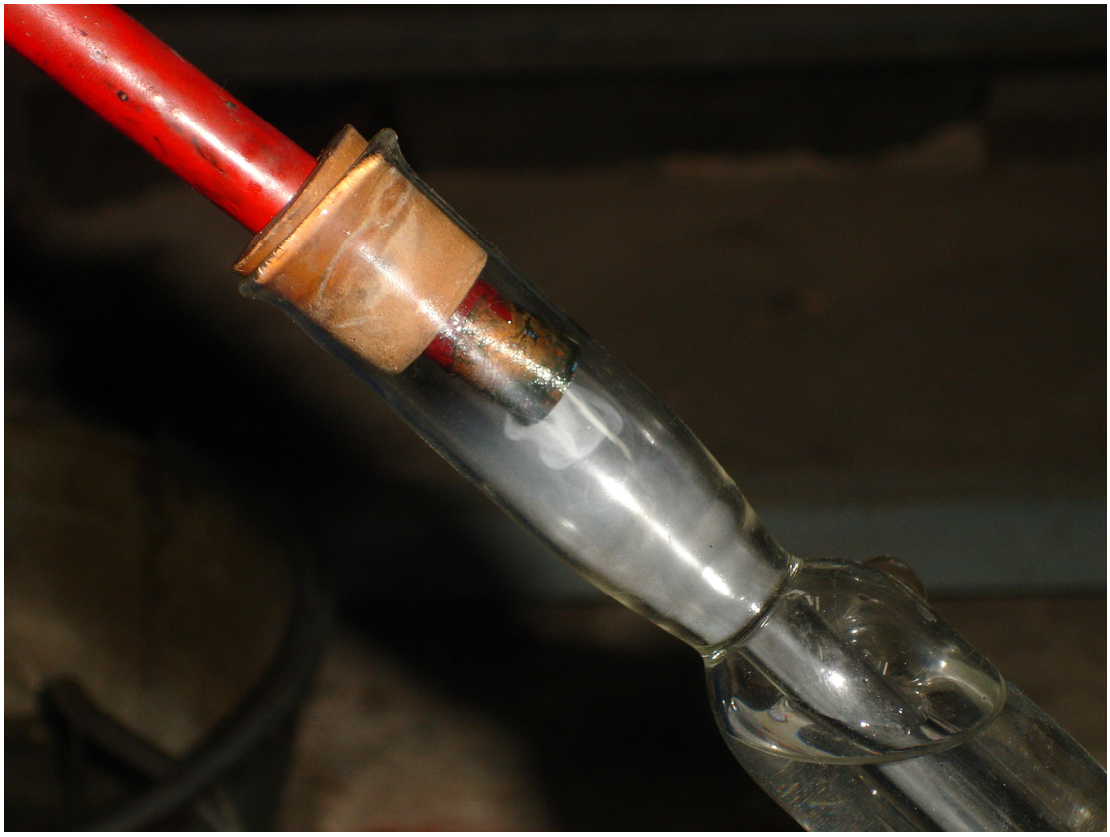


Fig 3.4: The vapours of cracked plastic moving into the glass condenser for condensation.

3.2.2 Catalytic Cracking

The same process that was followed during thermal cracking was followed here also. The only difference was that the catalyst in weighed amount was fed along with the plastic pellets.

The following catalysts were used for the pyrolysis process:

1. Silica Aluminate
2. Modernite
3. Activated Carbon

Thus the reaction inside the reactor takes place along with the catalyst and the vapours coming out is product of catalytic cracking. The vapours are passed into the glass condenser to be condensed to liquid. The liquid product is collected. The temperature maintained during catalytic cracking is much lower than that maintained during thermal cracking.

3.3 Analysis of Liquid Products

According to the literature that we went through, the liquid fuel products obtained contains mostly paraffins, olefins, naphthenes and aromatics (PONA). But due to economical reasons we were not able to find their composition. So, we selected to measure the physical properties like specific gravity, pour point, flash point etc.

3.3.1 Specific Gravity

The specific gravity was found out by using a 10 ml specific gravity bottle. 10 ml of the sample was taken in a pipette and the pre-weighted bottle was filled with the fuel sample to its brim. The final weight of the bottle was taken. This gave the weight of the sample which when divided by 10 to give the specific gravity and hence the density of the sample.

3.3.2 Pour Point

For finding the pour point, the sample was taken in a test tube and kept in an Ultra Low Temperature Refrigerator. The refrigerator has a capacity of giving temperature up to -85°C. After every 5°C drop in temperature, the sample was taken out and its fluidity was checked. At a particular temperature the liquid ceases to flow, this temperature was taken as the pour point of the fluid.

3.3.3 Flash Point

The flash point of the sample was determined by using Pensky Martin Apparatus. About 30 ml of the sample was taken in the cup of the apparatus and it was cooled by using a water bath. Continuous stirring was done during the process. After every 1°C fall in temperature, the vapour of the sample was exposed to a flame. The point at which fire starts with a flash is known as the flash point.

Chapter 4

Results and Discussion

4. Results and Discussion

The experiments on pyrolysis were conducted by using HDPE as the raw material. Both thermal cracking and catalytic cracking was done. The plastic was cracked thermally at various temperature ranges of 575ºC, 600ºC, 625ºC, and 650ºC. The products obtained were of different composition and the product yield was different for different temperatures. For catalytic cracking the catalysts used were silica alumina, modernite, activated carbon and aluminum silicate. The experiments were conducted by using different feed to catalyst ratios of 1:1, 2:1, 3:1, and 4:1. All these ratios required different temperature conditions and different time ranges. The liquid product yield varied for all these conditions.

4.1 Thermal Cracking

Cracking of plastic without using any catalyst yielded good amount of liquid product but the only problem was that the product solidified after settling for some time.

Temperature in º C	%Solid	%Liquid	%Gases	Nature of liquid product
600	2.85	50	47.15	Solidified liquid fuel
625	2.85	64.7	32.45	Solidified liquid fuel
650	2.85	78	19.15	Solidified liquid fuel

Table 4.1: Product composition for different temperature ranges of thermal cracking.

Fig 4.1: Solidified liquid product

4.2 Silica Alumina cracking

Silica Alumina is white amorphous powdery catalyst. It consists of 87% SiO_2, 13% Al_2O_3. From the SEM test of catalyst it can be seen that the catalyst has large number of pores in its structure, therefore its surface area for catalysis reaction is more. But again the pores are very large in size, which reduces its activity a bit.

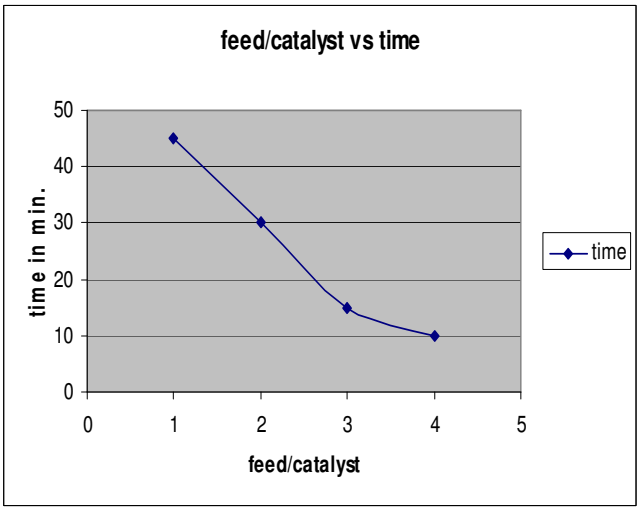
Catalyst	Ratio	%Solid	%Liquid	%Gases
Silica Alumina	1	3.167	58.33	38.503
Silica Alumina	2	3.167	66.67	30.163
Silica Alumina	3	3	78.57	18.43
Silica Alumina	4	3.27	54.54	42.19

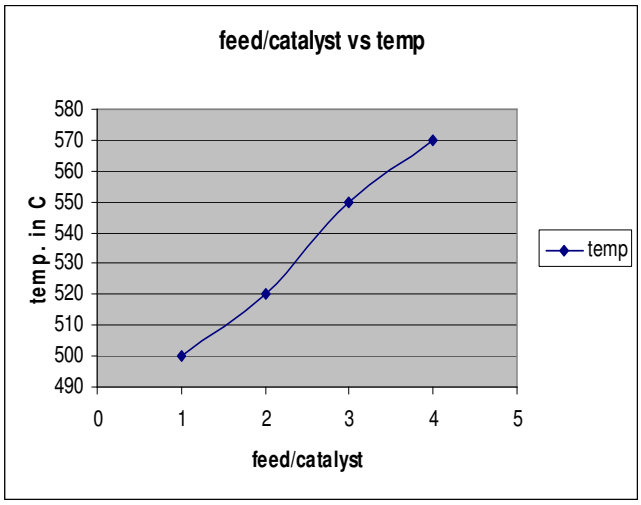
Table 4.2: Product composition for different catalyst ratio of silica alumina.

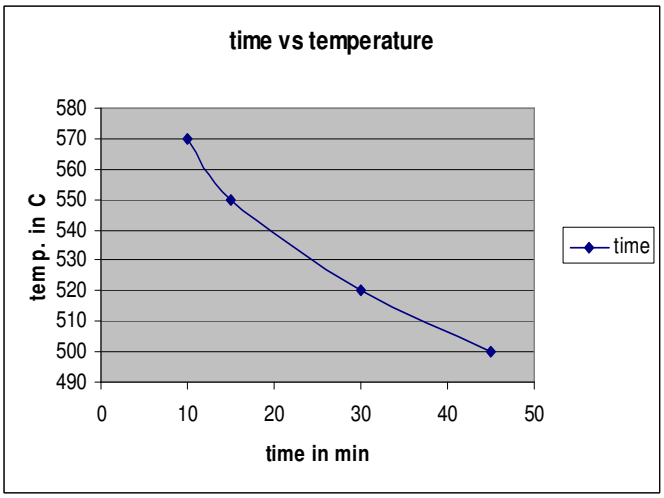
Feed	Catalyst	feed/catalyst	temp	Time	liquid product	% yield
55	14	4	570	10	30	54.54545
70	23.5	3	550	15	55	78.57143
60	30	2	520	30	40	66.66667
60	60	1	500	45	35	58.33333

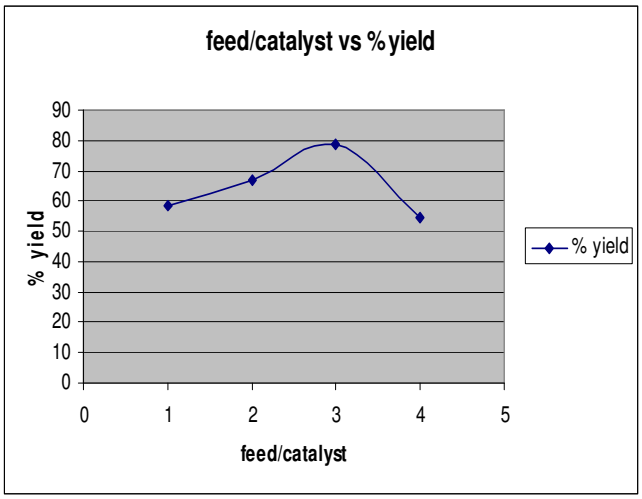
Table 4.3: The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products.

The different trends of the product obtained and its relation with time, temperature, amount of catalyst used is shown below.









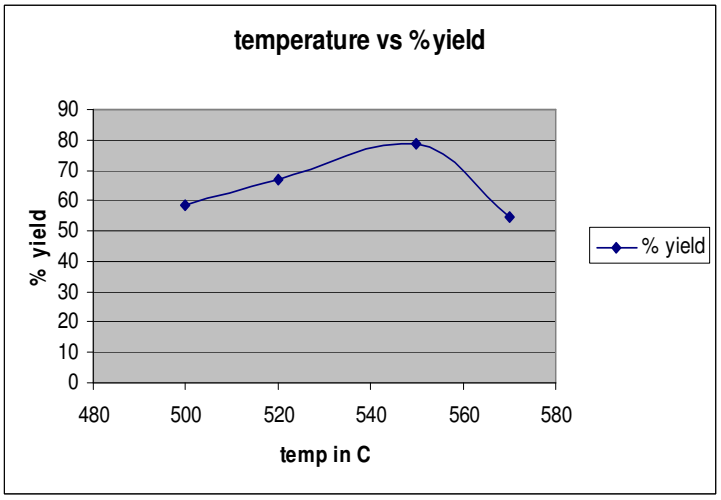


Fig 4.2: Relation of yield of product with time, temperature and feed/catalyst ratio for silica alumina.

4.3 Modernite cracking

Modernite is white coloured lumpy catalyst. It consists of 91.7% SiO_2, 8.23% Al_2O_3 and 0.03% Na_2O_3. From the SEM test of catalyst it can be seen that the catalyst has very less number of pores in its structure, therefore the surface area for catalysis reaction is less.

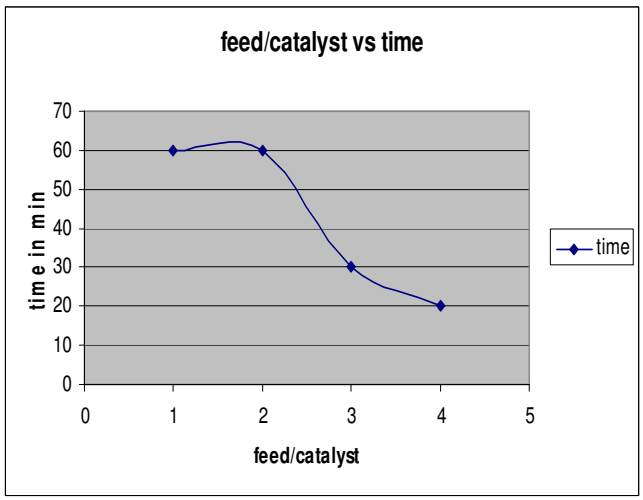
Catalyst	Ratio	%Solid	%Liquid	%Gases
Modernite	1	3.2	76	20.8
Modernite	2	3.167	56.67	40.163
Modernite	3	3.2	60	36.8
Modernite	4	3.2	80	16.8

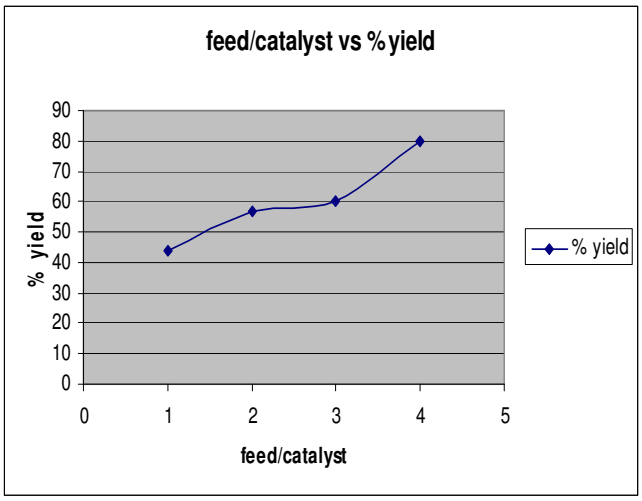
Table 4.4: Composition for different catalyst ratio of modernite.

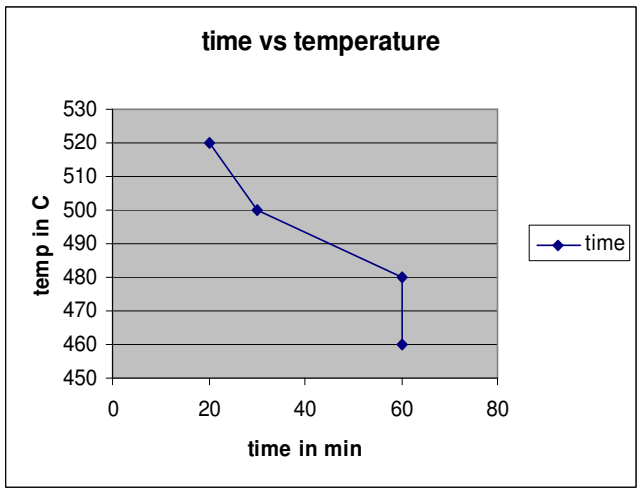
feed	catalyst	feed/catalyst	temp	time	liquid product	% yield
50	12.5	4	520	20	40	80
50	16.66	3	500	30	30	60
60	30	2	480	60	34	56.66667
50	50	1	460	60	22	44

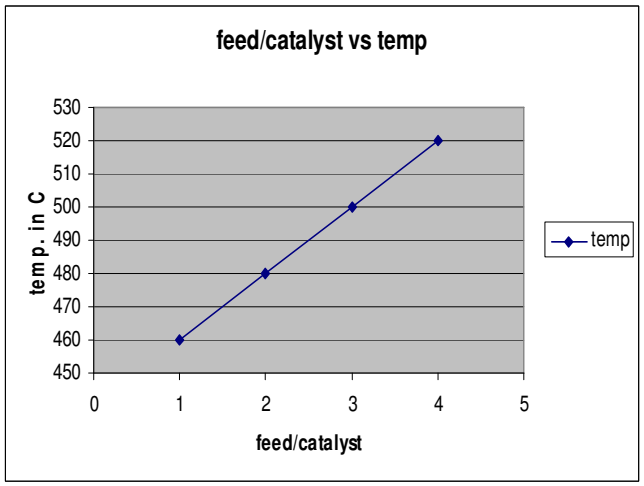
Table 4.5: The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products.

The different trends of the product obtained and its relation with time, temperature, amount of catalyst used is shown below.









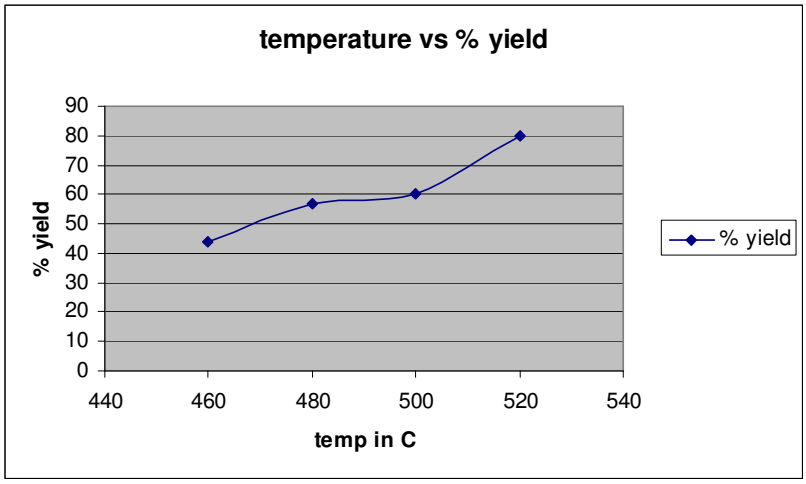


Fig 4.3: Relation of yield of product with time, temperature and feed/catalyst ratio for modernite.

4.4 Activated Carbon cracking

Activated carbon is black granular catalyst. It constitutes of carbon particles. From the SEM test it can be found out that activated carbon contains some amount of pores which are filled up after use. Thus, if activated carbon is reused again then it cannot yield good product.

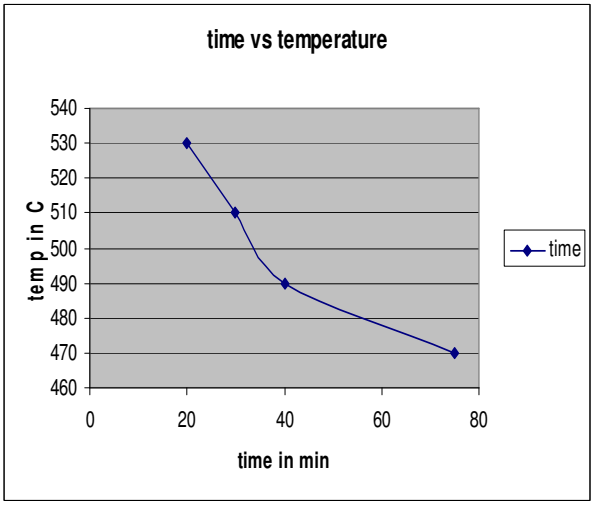
Catalyst	Ratio	%Solid	%Liquid	%Gases
Activated Carbon	1	3.09	72.72	24.19
Activated Carbon	2	3.2	74	22.8
Activated Carbon	3	3.2	74	22.8
Activated Carbon	4	3.2	64	32.8

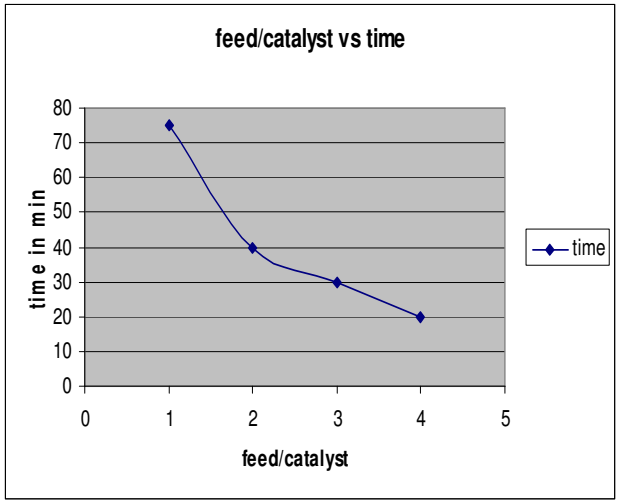
Table 4.6: Product composition for different catalyst ratio of silica alumina.

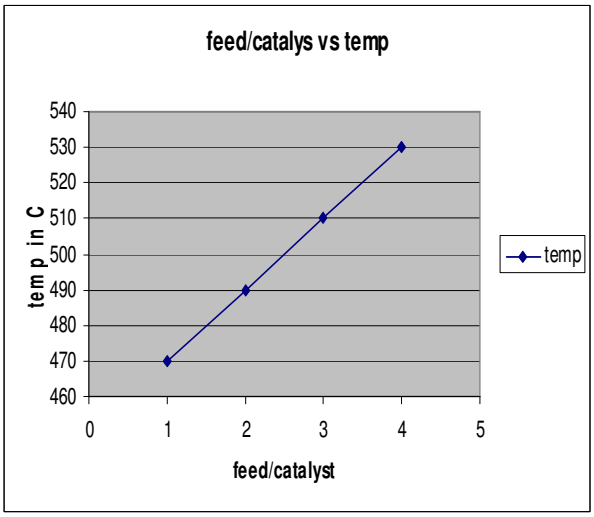
Feed	catalyst	feed/catalyst	temp	time	liquid product	% yield
50	12.5	4	530	20	32	64
50	16.66	3	510	30	37	74
50	25	2	490	40	37	74
55	50	1	470	75	40	72.72727

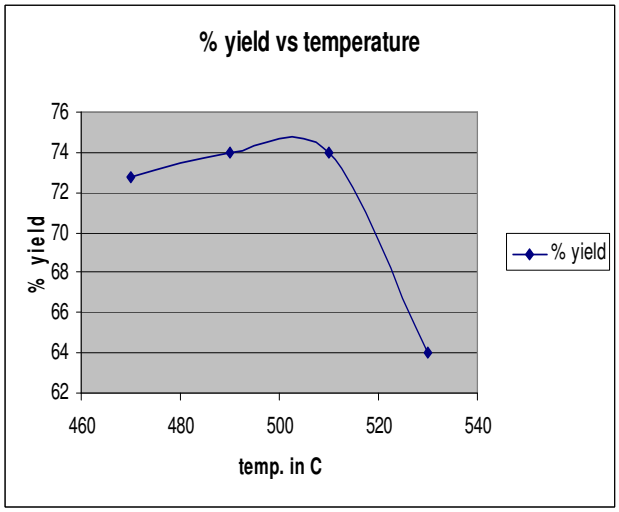
Table 4.7: The feed to catalyst ratio, time required for conversion, temperature needed and the percentage yield of liquid products.

The different trends of the product obtained and its relation with time, temperature, amount of catalyst used is shown below.









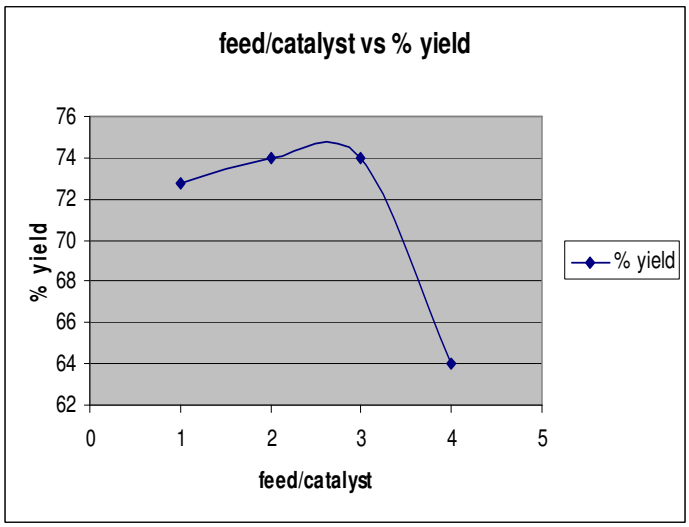


Fig 4.4: Relation of yield of product with time, temperature and feed/catalyst ratio for activated carbon.

The figures below shows the catalysts before use and after use.

Fig 4.5: Silica Aluminate (a) before use (b) after use

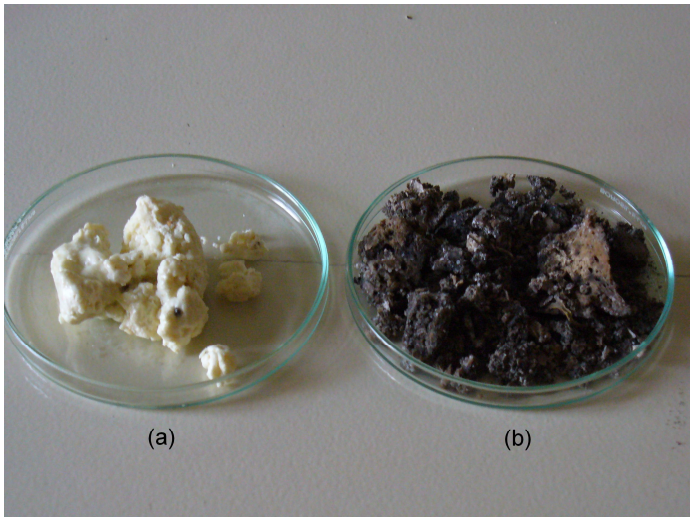


Fig 4.6: Modernite (a) before use (b) after use

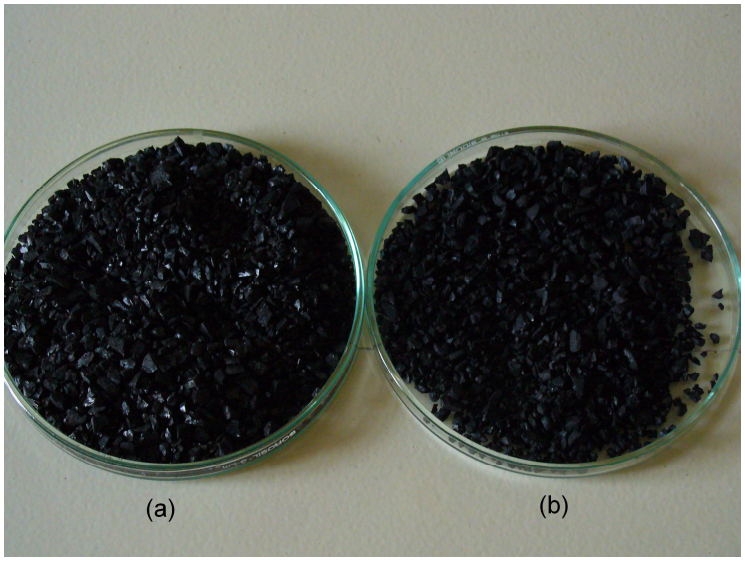


Fig 4.7: Activated Carbon (a) before use (b) after use

4.5 Product composition for different experiments

Different composition of liquid product was obtained for different catalyst and its different ratio with plastic feed. The liquid obtained was highest for a particular ratio at a particular temperature. This was the optimum range for the particular catalyst. It was seen that Alumina Silicate gave the maximum liquid product and it was the minimum for thermal cracking. The quality of product obtained was also better in case of catalytic cracking. In every process about 2% of carbon was obtained as final residue.

Fig 4.8: Different liquid products samples obtained during cracking

Fig 4.9: Solid carbon residue obtained after cracking

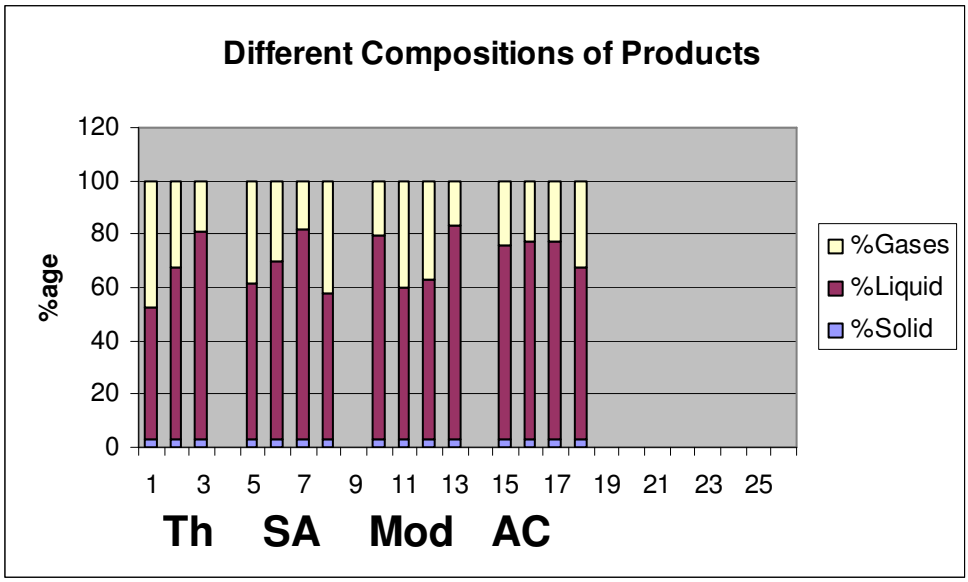


Fig 4.10: Composition of products obtained during various experiments

Th-Thermal cracking
SA- Silica Alumina cracking
Mod-Modernite cracking
AC-Activated Carbon cracking

4.6 Physical properties of different samples

The samples collected were tested for the physical properties like specific gravity, pour point and flash point.

The table below shows the different measured physical properties of the samples.

Catalyst	Ratio	Specific Gravity	Pour Point C	Flash Point C
Silica Alumina	1	0.7781	-60	31.5
Silica Alumina	2	0.7638	-60	31.5
Silica Alumina	3	0.7787	-60	31.5
Silica Alumina	4	0.7850	-60	31.5
Modernite	1	0.7625	-80	32
Modernite	2	0.7540	-80	32
Modernite	3	0.7754	-80	32
Modernite	4	0.7432	-80	32
Activated Carbon	1	0.8506	-80	31
Activated Carbon	2	0.8476	-80	31
Activated Carbon	3	0.8432	-82	31
Activated Carbon	4	-	-	-

Table 4.8: The different measured physical properties of the samples collected.

From the literature [20] it was found out that the specific gravity of gasoline varies from 0.72-0.75 and that of diesel oil is 0.82. The specific gravity of the samples prepared by us varies in that range. Thus it can be inferred to be of gasoline range fuel. The flash point of gasoline is 7°C and that of diesel oil lies between 60°C-80°C. The flash point the sample prepared lie in the range of 30-32. Thus the fuel may lie in between the range of gasoline and diesel oil.

Chapter 5

Conclusion

Conclusion

The waste plastic was subjected to various condition of reactions starting from thermal cracking to catalytic cracking by using different ratio of feed to catalyst. The product obtained in each case varied from the other in terms of yield of liquid product or in their physical properties. Again the temperature and time required in each case was different for all.

In case of thermal cracking the process yielded good amount of product. But the only problem was that it solidified completely after sometime. This may be because it was subjected to excess temperature. It was observed in this case that for first few minutes, good quality of product was evolved, but suddenly after a certain time impure product was obtained. This led to the solidifying of the product.

When the plastic was catalytically cracked by using Silica Alumina as the catalyst, it gave quite good quantity and quality of liquid fuel. The highest yield was obtained when the feed to catalyst ratio was 3:1. At this condition, it required a temperature of about 550°C and 15 minutes time. The liquid product obtained had a specific gravity of 0.7787 which is quite good and falls in the range of gasoline fuel. From the graph plotted for Silica Alumina, it can be observed that as the feed to catalyst ratio increases, the time of reaction decreases but the temperature required is more.

In case of using Modernite as the catalyst, the maximum yield of liquid product was obtained when the feed to catalyst ratio was 4:1. The second largest yield was when the ratio was 1:1. Thus we can infer that in this case too much catalyst may cause negative catalysis reaction. At 4:1 condition the time required was less but temperature required was more. The specific gravity of the liquid product obtained was in the range of gasoline.

If activated carbon was used, then maximum product yield was obtained when the ratio of feed to catalyst was 2:1 and 3:1. In the first case time required was more but less temperature was required but in the second case more temperature was required. The specific gravity of this product was higher then that of gasoline.

Thus from all the experiments we have performed, it can be inferred that the maximum yield of liquid fuel product was obtained when modernite was used in the ratio of 1:4 with the feed.

The liquid product was very much combustible and its specific gravity varied in the range of gasoline and diesel oil. Thus it can be inferred to be of gasoline range fuel. The flash point of

gasoline is 7°C and that of diesel oil lies between 60°C-80°C. The flash point the sample prepared lie in the range of 30-32. Thus the fuel may lie in between the range of gasoline and diesel oil.

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